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Dynamics of laser-induced cesium atom desorption from porous glass

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Abstract

The dynamics of short pulsed infrared laser-induced desorption of Cesium atoms from porous silica samples has been investigated. We find most probable kinetic energies of 69 ± 6 meV for desorption laser fluences between 60 and 190 mJ/cm^2, significantly higher compared to those obtained for Cs desorption from plain glass, 40 ± 2 meV, but lower compared to those observed for Na and Rb desorption from polymeric surfaces, 200 meV. This is explained qualitatively by scattering of the desorbing atoms with the silica nanochannels, thus suggesting different pulsed laser photodesorption processes for atoms embedded in hard porous dielectrics as compared to polymeric thin films.

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1. Introduction

Photo-desorption of alkali atoms from organic films, caused by weak intensity (<1 mW/cm^2) visible radiation and named LIAD [1] (light-induced atomic desorption) has been thoroughly investigated in the past, mainly in closed cell systems [2]. Organic films investigated so far include poly-dimethylsiloxane (PDMS), octamethylcyclotetrasiloxane (OCT) [3] and paraffine [4]. The overall characteristics of the effect (light power dependence and long-term temporal behaviour) were very similar, although the chemical compositions of the organics are rather different. This leads to the conclusion that LIAD is independent of the chemical composition and depends more on physical parameters such as sticking and diffusion probability inside the organics, state of the organics (i.e., rubbery, solid or glassy) etc. However, most of the experiments have been performed in closed cell systems with a quasi-equilibrium between ambient alkali gas atmosphere, alkali density inside the organics and gas pressure of the solid alkali source. Especially the long-term temporal behaviour in such systems is dominated by the gas pressure outside the solid and is as such not very sensitive to the desorption dynamics from or the binding mechanisms inside the solid.

In order to obtain a closer insight into the binding mechanism of the alkalis to the organics we have performed pulsed laser desorption measurements on alkali-loaded PDMS [5], using infrared and green pulsed laser radiation (pulse length 7 ns). The experiments have been performed both under normal incidence irradiation and under polarized evanescent wave excitation, the latter allowing us to discriminate between desorption from inside the organic film (where it in fact occurs) vs. desorption from the surface of the film. After loading the sample in a quasi-equilibrium alkali atmosphere the desorption experiments were made under non-equilibrium conditions in a separate vacuum chamber. We have found that LIAD under those conditions differs from conventional photodesorption in that it cannot be explained solely by indirect (thermal) or direct (electronic transitions induced) mechanisms. The model that we propose for the photo-desorption of alkalis from organic coatings [6] includes an electronic excitation induced transition into an antibinding surface state with

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low threshold. The final kinetic energy of the desorbing particles is dictated by the energetic positions of the involved potentials, but also by the thermal population of the individual states. An increase in sample temperature via resonant laser heating leads directly to an increase in kinetic energy of the desorbing particles.

Such a model is via the characteristic potentials involved specific to the alkali that has been bound to the organic. It is thus not surprising that the most probable kinetic energies of sodium (Na) atoms being desorbed under the same conditions from PDMS as rubidium (Rb) atoms, vary between 224 meV for Na [6] and 200 meV for Rb [7]. In Ref. [7] we have demonstrated that locally excited desorption from organic films can also be used to determine the diffusion coefficient for alkali atoms inside the organics. This demonstrates that although the experiments have been performed in the high-power regime the intensity of the desorbed particles is dictated by diffusion inside the organics and thus confirms the importance of coupling to the phonons of the organics for this special desorption process.

Recently it has been discovered in closed cell experiments that LIAD characteristics can also be observed for inorganics with a large internal surface, namely porous glass [8]. Porous glass is obtained by chemically removing part of a starting glass mixture and leaving a porous silica skeleton. The resulting silica pieces contain narrow and long tunnels where particles can be adsorbed and diffuse. In order to investigate whether this material could serve as a compact atom storage, nano-porous silica samples were placed inside Pyrex sealed cells filled with alkali atoms and then exposed to laser light. Under continuous-wave illumination the atoms embedded inside the glass matrix are ejected out of the sample causing an increase of the atomic density in the vapor phase. The photo-ejection is obtained even with non-coherent, weak light, just as in the case of LIAD from polymer films. The desorption efficiency has been studied as a function of laser light intensity and illumination time and again the results are similar to those obtained in cells coated with organic films. Even the dependence of desorbing rate and maximum density increase on laser light intensity shows the same behaviour as observed for LIAD from siloxane surfaces.

As noted above, these analogies are expected since the LIAD effect in cells is largely dominated by gas phase properties and by light-assisted diffusion inside the material. On the other hand, it was observed that the dynamic evolution of the intensity of photo-desorbed particles from porous glass shows some different features for varying desorbing light intensities and frequencies [9] that are not observed for organic coatings.

In order to find out whether the microscopic desorption mechanisms are similar for ‘porous’ organics and nano-porous inorganics, we have performed pulsed laser desorption experiments from porous glass under ultrahigh vacuum conditions. We have used embedded Cesium (Cs) atoms in order to complete the series of microscopic investigations on various alkalis. Reference measurements on Cs desorption from plain glass demonstrate the importance of the porous surface area for the desorption mechanism.

2. Experimental

The principle of the measurements is shown in Fig. 1a. First, the porous glass sample was loaded with Cs atoms in a vacuum chamber with 5×10^{-7} mbar residual pressure connected to a heated reservoir containing a few grams of metallic Cesium. The partial pressure of Cs vapor is expected to be 5×10^{-5} to 1×10^{-4} mbar in the 65–75 °C range, but adsorption on the stainless steel chamber walls would lower this value significantly to the 10^{-7} mbar level. To avoid this problem, the walls and windows of the chamber were also heated. The filling procedure took a few hours to a few days. Longer deposition times resulted in the formation of a metallic layer on the porous glass surface.

After loading, the sample was transferred into a main chamber using a magnetically coupled transfer rod. It was then firmly mounted in vacuum onto a rotatable manipulator that could be cooled. Note that both vacuum chambers were usually separated by the closed valve. This solution allowed us to keep the main chamber walls and windows clean from Cs atoms, which is important for obtaining a well-defined desorption point for time-of-flight measurements.

The main chamber had a base pressure of 5×10^{-9} mbar. The desorbing light was provided by a Nd:YAG pulsed laser working at a wavelength of 1064 nm with 5 Hz repetition rate. The laser light fluence

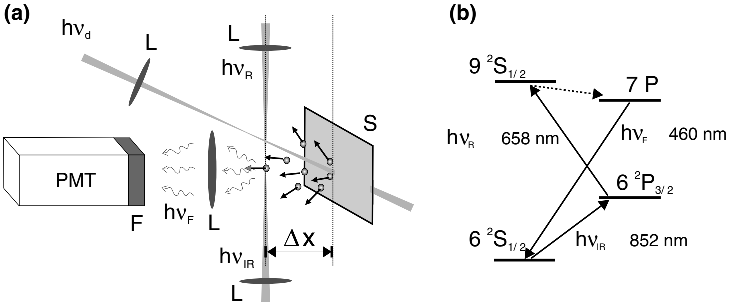

Fig. 1. (a) Sketch of the experimental set up. S: sample; F: interference filter; Δx: TOF distance; $h\nu_R$, $h\nu_{IR}$: detection beams, $h\nu_d$: desorption beam; $h\nu_F$: fluorescence photons; L: lens; PMT: photomultiplier and (b) Cs energy levels used for the TPLIF detection.

F was limited to 50–200 mJ/cm^2 in order to avoid damage of the porous glass via impurity absorption. The desorbing light spot radius on the sample was about 2 mm. Cs atoms were detected after desorption by the TPLIF (two-photon laser-induced fluorescence) method [10]. The relevant Cs energy levels are sketched in Fig. 1b. The excitation took place in the focal point of two counterpropagating continuous-wave laser beams generated by Littrow configuration diode lasers (TEC 100, Sacher). The 460 nm fluorescence photons were collected by a 277 K cooled photomultiplier (Hamamatsu R943-02) placed behind an infrared cut-off filter and an interference filter with 465 nm central frequency and 10 nm FWHM transmission width. Time-of-flight (TOF) measurements were performed using a multichannel analyzer triggered by the 7 ns desorption laser pulse. Distances Δx between the desorption laser spot on the sample and the detection focal point were chosen between 7 and 11 mm. The finite size of the detection area results in a 1 μs temporal resolution.

As a reference two-photon signal source, used for keeping the detection lasers on-line during the experiment, we have split the detection laser beams by beam splitters. The reference beams were aligned in the counterpropagating geometry, passing the filling chamber, where the two-photon fluorescence from Cs atoms was detected by a second photomultiplier.

Additional reference desorption measurements were done for a plain glass sample loaded by a thermal beam of atoms from a dispenser (Saes Getters). The temperature of the sample during loading and measurements was about 200 K to increase the sticking coefficients. Under those conditions the Cs atoms form rather a continuous, rough film on the glass surface.

3. Results and discussion

Time-of-flight (TOF) spectra for desorption of Cs atoms from porous glass are shown in Figs. 2 and 3. The best fits

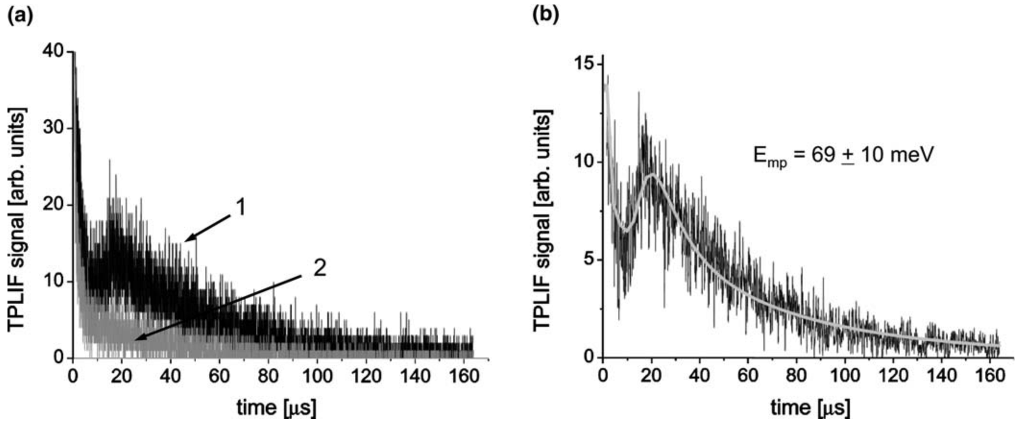

Fig. 2. TOF spectra for Cs atoms desorbed by 1064 nm pulses from porous glass: $F = 60$ mJ/cm^2, $\Delta x = 9.5$ mm. (a) Complete measured spectrum (curve 1) and background contribution (curve 2) obtained for one of the detection lasers out of resonance. (b) Smoothed signal after subtracting the background contribution. The fitted curve (Eq. (1) plus exponential decay) is shown as a solid line.

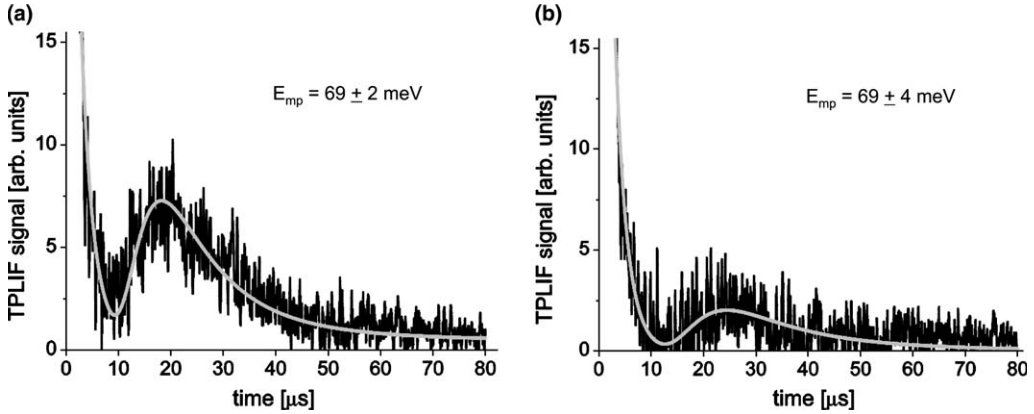

Fig. 3. TOF spectra for Cs atoms desorbed from porous glass with fitted curves given by Eq. (1) plus exponential decay: $F = 190$ J/cm^2 and $\Delta x = 8.2$ mm (a) as well as $\Delta x = 11$ mm (b).

to the data were obtained for flux-corrected Maxwell–Boltzmann distributions:

$$I(t) \sim t^{-4} \exp\left[-\frac{m\Delta x^2}{2t^2 k_B T}\right], \qquad (1)$$

where m is the Cs atomic mass, Δx the TOF distance, t the flight time, T the effective temperature of the distribution and k_B Boltzman's constant. The most probable kinetic energy is deduced from the fitted temperature via $E_{mp} = k_B T$. In addition to the Maxwell–Boltzmann distribution an exponential decay had to be implemented, representing the photomultiplier response to the residual infrared photons.

The results shown in Fig. 3 were obtained after careful cleaning of the sample with nitric acid solution and a small amount of sodium chlorate followed by baking under UHV conditions for several days at a temperature increased gradually to 150 °C [11]. We have found most probable kinetic energies $E_{mp} = 69 \pm 6$ meV for both desorption beam fluences of 60 and 190 mJ/cm^2. For comparison, a TOF spectrum for Cs atoms desorbed from plain glass is presented in Fig. 4. The best fit is given again by Eq. (1). The E_{mp} energy is found to be 40 ± 2 meV for fluences in the range 30–60 mJ/cm^2. This value is compatible with thermal desorption if one takes into account a slight heating of the substrate surface by photon absorption in the alkali-covered glass substrate.

Of course, whereas Cs forms a continuous rough film on plain glass at low temperatures in the case of porous glass we most probably deal with individual atoms trapped in the nano-channels. Thus it is more appropriate to compare our results with the previously obtained values of kinetic energies for alkali atoms desorbing from PDMS. As noted above, these values differ slightly from alkali to alkali, but in general are—at the present intensity level of the desorbing laser—of the order of 200 meV.

The significantly lower kinetic energy value for desorption from porous glass and its independence on laser intensity might be explained by one of the following models: (i) It might be due to a hot electron effect on the ionic bound alkalis with neutralization on their way out of the porous glass. A similar effect has been observed for photodesorption of potassium from amorphous silica [12], leading to kinetic energies of the order of 100 meV. However, since excitation of the ions requires high photon energies such an effect is more common for UV photons and less probable for IR photons. (ii) The effect might be similar to the photodesorption process described in Ref. [6] for pulsed laser desorption from PDMS. However, in the present case collisions with the walls 'cool down' the atoms to a certain degree on their way out of the nano-channels. In that case one would conclude that the temperature should depend on the thickness of the sample, which in principle is a quantity accessible to further experimental work.

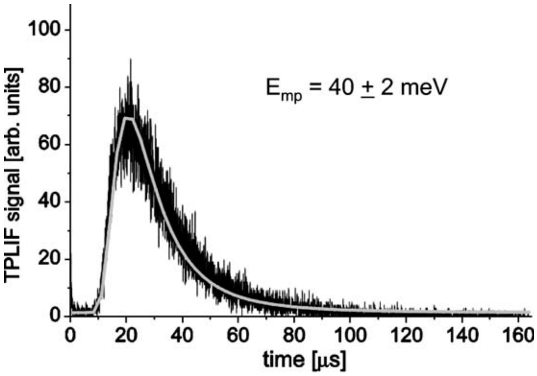

Fig. 4. TOF spectrum for Cs atoms desorbed from plain glass for $F = 60$ mJ/cm^2 and $\Delta x = 7.0$ mm (see text).

It is noted that both possible explanations result in kinetic energies independent of laser intensity since the initial laser adsorption process is rather decoupled from the final desorption event and thus is not responsible for the value of the final kinetic energy. We also point out that a more thorough explanation would have to take into account a possible difference in coverage for the different systems. This quantity is not available at present.

4. Conclusions

In this article we have measured the kinetics energies of Cs atoms desorbed via pulsed infrared light from porous glass. The energies are significantly higher compared to thermal desorption from plain glass but lower compared to 'conventional' LIAD from polymer films. This is qualitatively explained by electronic excitation, followed by scattering of the desorbing atoms inside the nano-channels of the porous medium.

Although the photodesorption process for embedded atoms from polymeric thin films is different compared to atoms desorbing from porous glass, both types of materials are equally important from an application point of view. In fact, the LIAD effect forms the basis of a chemically pure, light controllable source of alkali atoms and was as such used for fast and efficient loading of a magneto-optical trap [13]. It is worth noting that photodesorption from common glass with a relatively large surface area was also used for loading a surface magnetic trap and for achieving Bose–Einstein condensation in a cell experiment [14]. An inclusion of porous glass in such a set up could strongly improve the loading efficiency. In some way porous glass LIAD is the improved version of organic LIAD since it avoids problems with pollutants, delivers an even higher desorption efficiency and offers also the possibility to be structured into the micron- or sub-micron-regime by excimer laser ablation [15].

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